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PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

The Production of Phosphate Esters

We, GENERAL ANILINE & FILM CORPORATION, a corporation organized under the laws of the State of Delaware, United States of America of 140 West 51st Street, New York, New York, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement: —

This invention relates to a method of preparing alkali-soluble surface active compositions containing mixture of primary and secondary phospate esters of hydroxylic organic compounds.

It is known that hydroxylic compounds can be esterified with a number of different phosphating agents including phosphoric acid, P_2O_5, PCl_3 and $POCl_3$ and the like. The use of phosphoric acid or solutions of P_2O_5 in phosphoric acid as phosphating agent generally yields inconsistent mixtures of different types of esters, including esters of pyrophosphoric acid, phosphoric acid, primary, secondary and tertiary phosphates. When P_2O_5 has been employed, considerably greater molar ratios of the hydroxy compounds were regarded as necessary to bring the solid P_2O_5 into solution.

To eliminate the use of an excess of the hydroxylic organic compound, it has been proposed in U.S. Patent Specification 3,004,056 to react 1 mole of P_2O_5 with 2 to 4.5 moles of a non-ionic surface active agent derived from the condensation of at least 1 mole of an alkylene oxide with 1 mole of a hydroxylic organic compound under substantially anhydrous conditions at a temperature below about 110°C. Substantially no tertiary phosphate ester is formed by this process and little or no P_2O_5 remains in the composition. Depending upon the particular ratio of P_2O_5 to the non-ionic surface active agent employed, and the nature of such non-ionic surface active agent, the product contains from 30 to 80% of a primary ester, from 20 to 45% of secondary ester and from 0 to 40% by weight of unreacted non-ionic surface active agent which for certain uses is actually advantageous. The P_2O_5 is employed in dry, solid form as a granular powder or other finely divided or particulate form. In the phosphating reaction with the non-ionic surface active agent, the P_2O_5, however, may be first dispersed in an inert diluent such as benzene, xylene, ether, pentane or low and high boiling hydrocarbon fractions.

The phosphation reaction can advantageously be carried out in the presence of a small or catalytic amount of phosphorus-containing compound chosen from hypophosphorous acid, salts of hypophosphorous acid and salts and esters of phosphorous acid in an amount ranging from about 0.01 to 2% by weight based on the weight of the non-ionic surface active agent being phosphated as disclosed in U.S. Patent Specification 3,004,057. When hypophosphorous acid is employed, it is preferred to use a 30 to 50% aqueous solution thereof.

The phosphate esters of hydroxylic organic compounds prepared in accordance with the procedures described in U.S. Patent Specifications 3,033,889, 3,004,057 are all subject to the major disadvantages of being essentially insoluble in moderately concentrated solutions of aqueous alkali. This is true of practically all other surfactants such as oxyalkylene ethers of phenols or alcohols, or the sulfate esters of these ethers. Thus, their use in such operations as metal cleaning, Keir

boiling, bottle washing and as mercenizing assistants, has been severely limited.

According to this invention we provide a process for the preparation of phosphate esters of hydroxy group-containing compounds, which comprises reacting at a temperature between 20°C. and 145°C. a first component consisting of 1 mole of P_2O_5 as present in 110%—120% polyphosphoric acid with a second component consisting of 0.3 to 1.5 moles of (a) a primary aliphatic alcohol having from 3 to 20 carbon atoms inclusive, a cycloaliphatic alcohol having from 4 to 8 carbon atoms inclusive or an ethylene glycol monoalkyl ether wherein the monoalkyl group contains from 1 to 6 carbon atoms inclusive, or (b) a non-ionic surface active agent having the molecular configuration of a condensation product of at least 1 mole of an alkylene oxide of from 2 to 4 carbon atoms inclusive with 1 mole of a primary aliphatic alcohol having from 3 to 20 carbon atoms inclusive, a cycloaliphatic alcohol having from 4 to 8 carbon atoms inclusive, a phenol, an alkyl phenol, an aliphatic fatty acid having at least 8 carbon atoms or a polyglycol having a molecular weight between 1200 and 15,000, the said polyglycol being derived from a polypropylene glycol or substituted polypropylene glycol having a molecular weight of 300 to 3,000 and ethylene oxide, or (c) a non-ionic surface active agent which is derived from the reaction product of ethylene oxide and a water-insoluble polypropylene glycol containing a —$NHCH_2CH_2NH$— group or substituted polypropylene glycol having a molecular weight of 300 to 3,000.

The non-ionic surface active agent may, for instance, have the molecular configuration of a condensation product of 1 mole of ethylene oxide with 1 mole of *iso*octyl alcohol.

A small amount of hypophosphorous acid, or its salts, may be used for colour inhibition during the reaction. For instance, the process may be carried out in the presence of between 0.01% and 5% by weight of hyprophosphorous acid or a salt thereof or phosphorous acid or a salt or an ester thereof.

Because of the use of polyphosphoric acid, the resulting phosphate ester mixture is soluble to the extent of at least 1% in 13 to 30% aqueous solutions of caustic soda, potassium hydroxide, lithium hydroxide or ammonium hydroxide. The aqueous alkaline solutions of the phosphate ester mixture are especially adaptable as surface active agents in metal cleaning, Kier boiling, bottle washing, mercerizing operations and other cleaning and wetting applications where an aqueous alkaline solution of a surface active agents is a prime requirement.

In as much as the present invention is applicable as an improvement of the processes disclosed in U.S. Patent Specifications 3,004,056, 3,004,057 and 3,033,899, the same non-ionic surface active agents employed as reactants in the phosphation reaction, the same conditions of reaction, and the same manner of carrying out the reaction apply in the process of the invention which uses 110%—120% polyphosphoric acid as the phosphating agent.

As noted above, the aliphatic primary alcohols of from 3 to 20 carbon atoms inclusive include propanol, butanol, octanol, decanol, octadecanol and pentanol. Suitable cycloaliphatic alcohols include cyclobutanol, cyclohexanol or cycloheptanol and there may also be used ethylene glycol monoalkyl ethers wherein the alkyl ether contains from 1 to 6 carbon atoms such as ethylene glycol-monomethyl ether, -monoethyl ether, -monopropyl ether, -monobutyl ether, -monoamyl ether and -monohexyl ether. The branched chain aliphatic alcohols which may be used *in lieu* of straight chain primary aliphatic alcohols are those of the type incorporated in U.S. Patent Specification 3,033,889.

The polyphosphoric acid utilized as the phosphating agent in accordance with the present invention is an equilibrium mixture of *ortho*phosphoric, pyrophosphoric and higher linear phosphoric acids. The polyphosphoric acids commercially available range from 110% to 120% H_3PO_4 and contain from about 80% to 86.5% P_2O_5. Superphosphoric acid is equivalent to 105% H_3PO_4 containing 76% P_2O_5. Ordinary phosphoric acid ranges from 75% to 85% H_3PO_4 containing 54 to 61.5% of P_2O_5. The following Table shows, by commercial analysis, the percent of the H_3PO_4 content as well as the percent of P_2O_5 available in 110% to 120% polyphosphoric acid.

H_3PO_4 Content %	P_2O_5%	$\frac{H_2O}{P_2O_5}$ (Mol.)
110% melt	79.5	1.97
113% melt	81.6	1.78
115% melt	83.0	1.61
117% melt	84.5	1.44
120% melt	86.5	1.23

The non-ionic surface active agents employed as reactants with the 110%—120% polyphosphoric acid are well known in the art. In general, they are obtained by reacting at least 1 mole of a C_2—C_4 alkylene oxide such as ethylene oxide, propylene oxide or butylene oxide with 1 mole of an aliphatic alcohol, phenol, alkylated phenol or aliphatic fatty acid. Numerous compounds of this type are described in U.S. Patent Specifications 2,213,477 and 2,593,112, which describe polyalkylene oxide derivatives of phenolic compounds in which the total number of alkyl carbon atoms is between 4 and 20. As examples of such phenolic compounds

may be mentioned normal and isomeric butyl, amyl, dibutyl, and diamyl phenols and cresols, tripropyl phenols and cresols, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tetradecyl, cetyl, oleyl, or octadecyl, phenols and cresols in addition to dihexyl- and trihexyl-phenol prepared from hexene-1 and phenol, di*iso*-heptyl-phenol, dioctyl-phenol, dinonyl-phenol, dioctyl-*p*-cresol, dioctyl-*o*-cresol, didecyl-phenol, didecyl - *p* - cresol or didodecyl - phenol. Of particular value are the polyalkylene oxide derivatives of secondary and tertiary alkyl substituted phenols and cresols obtained by condensing olefines of the type obtained in petroleum refining with phenols or cresols. In the case of products obtained by condensing phenol or cresol with olefines of from 3 to 5 carbon atoms inclusive such as propylene, butylene or amylene, it is sometimes desirable to employ the dialkylated phenols or cresols, while in the case of compounds obtained by condensing a phenol or cresol with an olefine containing 8 or more carbon atoms, the mono-substituted derivatives are sometimes preferred. Particularly desirable derivatives can be obtained from the phenols and cresols containing a substituent derived from olefins containing from 8 to 18 carbon atoms inclusive such as di*iso*butylene and other alkylenes such as nonylene, decylene, undecylene, dodecylene, pentadecylene, octadecylene and mixture thereof, and may advantageously be the dimers and trimers obtained by polymerization of such low molecular weight olefines as propylene, butylene, *iso*butylene, amylene or mixtures thereof.

The polyalkylene oxide derivatives described in U.S. Patent Specification 1,970,578 are particularly adaptable to the method of the present invention. As examples of aliphatic fatty acids, both saturated and unsaturated, whose polyalkylene oxide derivatives may be phosphated in accordance with the present invention may be mentioned those derivatives prepared from caprylic, lauric, oleic, ricinoleic, palmitic, stearic, behenic acid or erucic acid and mixtures thereof, such as the mixtures obtained from animal and vegetable fats and oils or by the oxidation of such petroleum fractions as paraffin wax.

Another group of non-ionic surface active agents which may be phosphated are those of the Pluronic type as disclosed for example in U.S. Patent Specification 2,674,619 and other patent Specifications. "PLURONIC" is a Trade Mark. In general, in preparing these agents a suitable 1,2-alkylene oxide or substituted alkylene oxide, as for example butylene oxide, amylene oxide, phenyl ethylene oxide (oxystyrene), cyclohexene oxide, cyclooctene oxide or preferably propylene oxide, or a mixture thereof, is polymerized in the presence of an alkaline catalyst such as sodium hydroxide, preferably at elevated temperatures and pressures to produce the corresponding water-insoluble polypropylene glycol or substituted polypropylene glycol having a molecular weight of 300 to 3,000. The resulting polyglycol is then reacted under similar conditions with the required number of moles of ethylene oxide to yield the desired non-ionic surface active agent which is then phosphated. These polyglycols should generally have a molecular weight ranging from 1,200 to 15,000 and preferably 2,000 to 10,000. Alternatively, ethylene diamine, propylene diamine, other alkylene diamines and polyalkylene polyamines, or ethylene glycol, propylene glycol, 1,4-butanediol, hexamethylene glycol and other diols may be reacted with the required number of moles of propylene oxide or substituted propylene oxide to produce the corresponding water-insoluble polypropylene glycols containing a —$NHCH_2CH_2NH$— group and substituted polypropylene glycols having a molecular weight of about 300 to 3,000 as described above, followed by reaction with the required number of moles of ethylene oxide. These "Pluronic" types of nonionic surface active agents will ordinarily be of the diol type containing two terminal hydroxy (ethanol) groups. Both of these terminal hydroxy groups may be alkoxylated, preferably ethoxylated, and then phosphated in accordance with the present invention.

The following examples, of which Examples XXI to XXIV are intended for comparison purposes, are illustrative of the preparation of phosphate esters of various aliphatic alcohols, ethylene glycol monoalkyl ethers or alkylated phenols which are phosphated in accordance with the process of the invention to yield surface active compositions having solubility in moderately concentrated aqueous alkali.

In these Examples the reaction product consists of a mixture containing from 70% to 90% of monoester, from 9% to 28% of diester and from 0.1% to 12% of unreacted non-ionic surface active agent or unreacted aliphatic alcohol. These components are characterized by the following general formulae:

$$R{-}(OCH_2CH_2)_n{-}O{-}\overset{\overset{O}{\|}}{P}{-}OH \quad\text{with } P{-}OH$$

monoester

$$\left[R{-}(OCH_2CH_2)_n{-}O{-}\right]_2 \overset{\overset{O}{\|}}{P}{-}OH$$

diester

$$R-(OCH_2CH_2)_n-OH,$$

unreacted nonionic surface active agent or unreacted aliphatic alcohol wherein R is the residue of an aliphatic or aromatic compound which contained a reactive hydrogen atom or the residue of an aliphatic alcohol, and n is 0 to 20 inclusive.

EXAMPLE I

A total of 340 grams of 115% polyphosphoric acid (containing 2 moles of P_2O_5) were added to 436 grams (2.0 moles) of the condensation product of one mole of *iso*-octyl alcohol with 2 moles of ethylene oxide over a period of one hour. Temperature was held below 70°C. with external cooling. Following the addition, the charge was heated to 90—95°C. and held at this temperature for four hours.

Product was soluble to the extent of 1% in 20% aqueous caustic soda.

% Monoester	=	89.8
% Diester	=	8.9
% Non-ionic	=	1.9

Wetting time (by the Standard Test Method 43-1952 of the American Association of Textile Chemists and Colorists)—3 min. at 1% in 20% NaOH.

EXAMPLE II

A total of 170 grams of 115% polyphosphoric acid (containing 1 mole of P_2O_5) were added to 598 grams (1.0 mole) of the condensation product of one mole of decyl alcohol with 10 moles of ethylene oxide in the presence of 2.0 grams hypophosphorous acid over a period of one hour. Temperature was held below 70°C. with external cooling. Following the addition, the charge was heated to 90—95°C. and held at this temperature for four hours.

Product was soluble to the extent of 1% in 13% aqueous caustic soda.

% Monoester	=	85.2
% Diester	=	12.1
% Non-ionic	=	2.9

EXAMPLE III

A total of 204 grams of 115% polyphosphoric acid (containing 1.2 moles of P_2O_5) were added to 580 grams (1.2 moles) of the condensation product of one mole of nonyl phenol with 6 moles of ethylene oxide over a period of one hour. Temperature was held below 70°C. with external cooling. Following the addition, the charge was heated to 90—95°C. and held at this temperature for four hours.

Product was soluble to the extent of 1% in 13% aqueous caustic soda.

% Monoester	83.5
% Diester	5.9
% Non-ionic	6.2

EXAMPLE IV

A total of 220 grams of 115% polyphosphoric acid (containing 1.3 moles of P_2O_5) were added to 605 grams (1.3 moles) of the condensation product of one mole of tridecyl alcohol with 6 moles of ethylene oxide over a period of one hour. Temperature was held below 70°C. with external cooling. Following the addition, the charge was heated to 90—95°C. and held at this temperature for four hours.

Product was soluble to the extent of 1% in 13% aqueous caustic soda.

% Monoester	77.8
% Diester	19.3
% Non-ionic	1.6

EXAMPLE V

A total of 127 grams of 115% polyphosphoric acid (containing 0.75 mole of P_2O_5) were added to 645 grams (0.75 mole) of the condensation product of one mole of tridecyl alcohol with 15 moles of ethylene oxide over a period of one hour. Temperature was held below 70°C. with external cooling. Following the addition, the charge was heated to 90—95°C. and held at this temperature for four hours.

Product was soluble to the extent of 1% in 13% aqueous caustic soda.

% Monoester	79.0
% Diester	9.0
% Non-ionic	11.9

EXAMPLE VI

A total of 170 grams of 115% polyphosphoric acid (containing one mole of P_2O_5) were added to 306 grams (0.5 mole) of the condensation product of one mole of nonyl phenol with 9 moles of ethylene oxide over a period of one hour. Temperature was held below 70°C. with external cooling. Following the addition, the charge was heated to 90—95°C. and held at this temperature for four hours.

Product was soluble to the extent of 1% in 13% aqueous caustic soda.

% Monoester	91.0
% Diester	8.7
% Non-ionic	0.6

EXAMPLE VII

A total of 170 grams of 115% polyphosphoric acid (containing one mole of P_2O_5) were added to 459 grams (0.75 mole) of the condensation product of one mole of nonyl phenol with 9 moles of ethylene oxide over a period of one hour. Temperature was held

below 70°C. with external cooling. Following the addition, the charge was heated to 90—95°C. and held at this temperature for four hours.

Product was soluble to the extent of 1% in 13% aqueous caustic soda.

% Monoester	89.4
% Diester	10.1
% Non-ionic	0.9

EXAMPLE VIII

A total of 170 grams of 115% polyphosphoric acid (containing one mole of P_2O_5) were added to 612 grams (1.0 mole) of the condensation product of one mole of nonyl phenol with 9 moles of ethylene oxide over a period of one hour. Temperature was held below 70°C. with external cooling. Following the addition, the charge was heated to 90—95°C. and held at this temperature for four hours.

Product was soluble to the extent of 1% in 13% aqueous caustic soda.

% Monoester	87.0
% Diester	9.3
% Non-ionic	4.2

EXAMPLE IX

A total of 170 grams of 115% polyphosphoric acid (containing one mole of P_2O_5) were added to 598 grams (1.0 mole) of the condensation product of one mole of *n*-decyl alcohol with 10 moles of ethylene oxide over a period of one hour. Temperature was held below 70°C. with external cooling. Following the addition, the charge was heated to 90—95°C. and held at this temperature for four hours.

Product was soluble to extent of 1% in 13% aqueous caustic soda.

% Monoester	74.0
% Diester	21.7
% Non-ionic	4.6

EXAMPLE X

A total of 340 grams of 115% polyphosphoric acid (containing 2 moles of P_2O_5) were added to 464 grams (2.0 moles) of the condensation product of one mole of cyclohexanol with 3 moles of ethylene oxide over a period of one hour. Temperature was held below 70°C. with external cooling. Following the addition, the charge was heated to 90—95°C. and held at this temperature for four hours.

Product was soluble to the extent of 1% in 13% aqueous caustic soda.

% Monoester	76.5
% Diester	20.1
% Non-ionic	9.2

EXAMPLE XI

A total of 510 grams of 115% polyphosphoric acid (containing 3 moles of P_2O_5) were added to 354 grams (3.0 moles) of the condensation product of one mole of butyl alcohol with 1 mole of ethylene oxide over a period of one hour. Temperature was held below 70°C. with external cooling. Following the addition, the charge was heated to 90—95°C. and held at this temperature for four hours.

Product was soluble to the extent of 1% in 30% aqueous caustic soda.

% Monoester	71.0
% Diester	27.2
% Non-ionic	0.1

Wetting time (by the Standards of AATCC STM 43—1952)—6 sec. at 1% in 20% NaOH
8 sec. at 1/2%

EXAMPLE XII

A total of 425 grams of 115% polyphosphoric acid (containing 2.5 moles of P_2O_5) were added to 405 grams (2.5 moles) of the condensation product of one mole of butyl alcohol with 2 moles of ethylene oxide over a period of one hour. Temperature was held below 70°C. with external cooling. Following the addition, the charge was heated to 90—95°C and held at this temperature for four hours.

Product was soluble to extent of 1% in 30% aqueous caustic soda.

% Monoester	73.8
% Diester	27.2
% Non-ionic	0.1

Wetting time (by the Standards of AATCC STM 43—1952) 7 sec. at 1% in 20% NaOH
20 sec. at 1/2%

EXAMPLE XIII

A total of 408 grams of 115% polyphosphoric acid (containing 2.4 moles of P_2O_5) were added to 370 grams (2.4 moles) of the condensation product of one mole of *iso*-amyl alcohol with 1.5 moles of ethylene oxide over a period of one hour. Temperature was held below 70°C. with external cooling. Following the addition, the charge was heated to 90—95°C. and held at this temperature for four hours.

Product was soluble to extent of 1% in 30% aqueous caustic soda.

% Monoester	78.0
% Diester	22.2
% Non-ionic	0.4

Wetting time (by the Standards of AATCC STM 43—1952) 24 sec. at 1% in 20% NaOH

EXAMPLE XIV

A total of 355 grams of 115% polyphosphoric acid (containing 2.1 moles of P_2O_5) were added to 416 grams (2.1 moles) of the condensation product of one mole of *iso*-amyl alcohol with 2.5 moles of ethylene oxide over a period of one hour. Temperature was held below 70°C. with external cooling. Following the addition, the charge was heated to 90—95°C. and held at this temperature for four hours.

Product was soluble to extent of 1% in 30% aqueous caustic soda.

% Monoester	75.8
% Diester	22.5
% Non-ionic	0.4

Wetting time (by the Standards of AATCC STM—1952) 24 sec. at 1% in 20% NaOH

EXAMPLE XV

A total of 340 grams of 115% polyphosphoric acid (containing 2 moles of P_2O_5) were added to 176 grams (2.0 moles) of *iso*-amyl alcohol over a period of one hour. Temperature was held below 70°C. with external cooling. Following the addition, the charge was heated to 90—95°C. and held at this temperature for four hours.

Product was soluble to extent of 1% in 20% aqueous caustic soda.

% Monoester	79.5
% Diester	14.7
% Alcohol	6.7

Wetting time (by the Standards of AATCC STM 43—1952) 4—6 sec. at 1% in 20% NaOH

EXAMPLE XVI

A total of 272 grams of 115% polyphosphoric acid (containing 1.6 moles of P_2O_5) were added to 122 grams (1.6 moles) of Methyl "Cellosolve" over a period of one hour. Temperature was held below 70°C. with external cooling. Following the addition, the charge was heated to 90—95°C. and held at this temperature for four hours. "Cellosolve" is a trade mark.

Product was soluble to the extent of 1% in 20% aqueous caustic soda.

% Monoester	76.6
% Diester	16.8
% Methyl "Cellosolve"	7.7

Wetting time (by the Standards of AATC STM 43—1952) 5 min. at 1% in 20% NaOH.

EXAMPLE XVII

A total of 272 grams of 115% polyphosphoric acid (containing 1.6 moles of P_2O_5) were added to 144 grams (1.6 moles) of Ethyl "Cellosolve" over a period of one hour. Temperature was held below 70°C. with external cooling. Following the addition, the charge was heated to 90—95°C. and held at this temperature for four hours.

Product was soluble to the extent of 1% in 20% aqueous caustic soda.

% Monoester	75.3
% Diester	19.6
% Ethyl "Cellosolve"	4.7

Wetting time (by the Standards of AATCC STM 43—1952) 5 min. at 1% in 20% NaOH.

EXAMPLE XVIII

A total of 170 grams of 115% polyphosphoric acid (containing 1 mole of P_2O_5) were added to 598 grams (1 mole) of the condensation product of 1 mole of *n*-decyl alcohol with 10 moles of ethylene oxide over a period of one hour. Temperature was held below 70°C with external cooling. Following the addition, the charge was heated to 140°—145°C. and held at this temperature for one hour.

Product was soluble to the extent of 1% in 13% aqueous caustic soda.

% Monoester	84.1
% Diester	14.2
% Non-ionic	1.7

EXAMPLE XIX

Example XVIII was repeated with the exception that following the addition, the charge was held at 30—35°C. for six hours.

Product was soluble to the extent of 1% in 13% aqueous caustic soda.

% Monoester	86.4
% Diester	11.3
% Non-ionic	3.1

EXAMPLE XX

A total of 170 grams of 115% polyphosphoric acid (containing 1 mole of P_2O_5) were added to 521 grams (1 mole) of the condensation product of 1 mole of oleic acid with 5.43 moles of ethylene oxide over a period of one hour. Temperature was held below 70°C with external cooling. Following the addition, the charge was heated to 90—95°C. and held at this temperature for four hours.

Product was soluble to the extent of 1% in 20% aqueous caustic soda.

% Monoester	81.0
% Diester	8.0
% Non-ionic	12.6

EXAMPLE XXI

A total of 212 grams of 115% polyphosphoric acid (containing 1.25 moles of P_2O_5)

were added to 654 grams (3.0 moles) of the condensation product of one mole of *iso*-octyl alcohol with 2 moles of ethylene oxide over a period of one hour. Temperature was held below 70°C. with external cooling. Following the addition, the charge was heated to 90—95°C. and held at this temperature for four hours.

Product was insoluble in 13% aqueous caustic soda.

% Monoester	77.0
% Diester	6.1
% Non-ionic	16.2

This Example shows that by deviation from the limits of mole ratio of the non-ionic surface active agents as used in the process of the solution, the resulting reaction product is insoluble in the aqueous caustic soda.

Example XXII

A total of 117 grams of 115% superphosphoric acid (containing 0.625 mole of P_2O_5) were added to 327 grams (1.5 moles) of the condensation product of one mole of *iso*-octyl alcohol with 2 moles of ethylene oxide over a period of one hour. Temperature was held below 70°C. with external cooling. Following the addition, the charge was heated to 90—95°C. and held at this temperature for four hours.

Product was insoluble in 13% aqueous caustic soda.

% Monoester	76.7
% Diester	—
% Non-ionic	33.2

Also this Example shows that a deviation from the limits of mole ratio of the non-ionic surface active agents prescribed above will make the resulting reaction product insoluble in aqueous caustic soda.

Example XXIII

A total of 187 grams of 105% superphosphoric acid (containing 1 mole of P_2O_5) were added to 598 grams (1.0 mole) of the condensation production of one mole of decyl alcohol with 10 moles of ethylene oxide in the presence of 2.0 grams hypophosphorous acid over a period of one hour. Temperature was held below 70°C. with external cooling. Following the addition, the charge was heated to 90—95°C. and held at this temperature for four hours.

Product was insoluble in 13% aqueous caustic soda.

% Monoester	54.0
% Diester	5.9
% Non-ionic	42.0

This Example shows that by employing a superphosphoric acid of a lower percent of P_2O_5 than that used in the process of the present invention, a reaction product is obtained which is insoluble in aqueous caustic soda.

Example XXIV

A total of 300 grams of 105% superphosphoric acid (containing 1.6 mole of P_2O_5) were added to 457 grams (1.6 mole) of the condensation product of one mole of nonyl phenol with 1.5 mole of ethylene oxide over a period of one hour. Temperature was held below 70°C. with external cooling. Following the addition, the charge was heated to 90—95°C. and held at this temperature for four hours.

Product was insoluble in 13% aqueous caustic soda.

% Monoester	69.8
% Diester	18.9
% Non-ionic	21.0

This Example shows that when employing superphosphoric acid of a lower percent of P_2O_5 than that used in the process of the present invention, the resulting reaction product is insoluble in aqueous caustic soda.

WHAT WE CLAIM IS:—

1. A process for the preparation of phosphate esters of hydroxy group-containing compounds, which comprises reacting at a temperature between 20°C and 145°C. a first component consisting of 1 mole of P_2O_5 as present in 110%—120% polyphosphoric acid with a second component consisting of 0.3 to 1.5 moles of (a) a primary aliphatic alcohol having from 3 to 20 carbon atoms inclusive, a cycloaliphatic alcohol having from 4 to 8 carbon atoms inclusive or an ethylene glycol monoalkyl ether wherein the monoalkyl group contains from 1 to 6 carbon atoms inclusive, or (b) a non-ionic surface active agent having the molecular configuration of a condensation product of at least 1 mole of an alkylene oxide of from 2 to 4 carbon atoms inclusive with 1 mole of a primary aliphatic alcohol having from 3 to 20 carbon atoms inclusive, a cycloaliphatic alcohol having from 4 to 8 carbon atoms inclusive, a phenol, an alkyl phenol, an aliphatic fatty acid having at least 8 carbon atoms or a polyglycol having a molecular weight between 1200 and 15,000, the said polyglycol being derived from a polypropylene glycol or substituted polypropylene glycol having a molecular weight of 300 to 3,000 and ethylene oxide, or (c) a non-ionic surface active agent which is derived from the reaction product of ethylene oxide and a water-insoluble polypropylene glycol containing a —$NHCH_2CH_2NH$— group or substituted polypropylene glycol having a molecular weight of 300 to 3,000.

2. The process as claimed in Claim 1, wherein the ethylene glycol monoalkyl ether of (a) is ethylene glycol monoethyl ether.

3. The process as claimed in Claim 1, wherein the primary aliphatic alcohol of (a) or (b) is *iso*amyl alcohol.

4. The process as claimed in Claim 1, wherein the non-ionic surface active agent (b) has the molecular configuration of a condensation product of 1 mole of ethylene oxide with 1 mole of *iso*ctyl alcohol.

5. The process as claimed in Claim 1, wherein the non-ionic surface active agent (b) has the molecular configuration of a condensation product of 6 moles of ethylene oxide with 1 mole of nonyl phenol.

6. The process as claimed in Claim 1, wherein the non-ionic surface active agent (b) has the molecular configuration of a condensation product of 1 mole of ethylene oxide with 1 mole of butyl alcohol.

7. The process as claimed in Claim 1, wherein the non-ionic surface active agent (b) is a condensation product of 1.5 moles of ethylene oxide with 1 mole of *iso*amyl alcohol.

8. The process as claimed in any preceding claim, which is carried out in the presence of between 0.01% and 5% by weight of hypophosphorous acid or a salt thereof or phosphorous acid or a salt or an ester thereof.

9. The process as claimed in Claim 1 substantially as herein described and exemplified.

10. Phosphate esters obtained by the process claimed in any preceding claim or an obvious equivalent thereof.

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